

Hydrolysis of Chlorpyrifos in Aqueous and Colloidal Systems

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Abstract. Hydrolysis of chlorpyrifos [*O,O*-diethyl *O*-(3,5,6-trichloro-2-pyridyl) phosphorothioate] to TCP (3,5,6-trichloro-2-pyridinol) is an important degradation process influencing the fate of chlorpyrifos in aquatic environments. The effects of water chemistry and suspended colloids (smectites, humic acid, and river sediment) on the hydrolysis of chlorpyrifos were investigated in this study. Chlorpyrifos was incubated in various aqueous and colloidal systems at 23 ± 2 °C for up to 100 days, and aqueous phase concentrations of chlorpyrifos and TCP were determined using solid phase extraction–high performance liquid chromatography (SPE–HPLC). Chlorpyrifos degraded in the aqueous solutions with half-lives ranging from 27 to 158 days, depending on the initial concentration of chlorpyrifos and the chemistry of the aqueous solutions. The rate of degradation was slower in systems containing low concentrations of suspended colloids (1 g L^{-1} in 0.01 M CaCl_2) than in the control (0.01 M CaCl_2 , with no colloids), and negligible hydrolysis of chlorpyrifos was found for concentrated colloidal systems (20 g L^{-1} in 0.01 M CaCl_2). Total recoveries of chlorpyrifos for the concentrated colloidal systems ranged from 78% to 97%, with a tendency to decrease with incubation time. The study indicates that the formation of chlorpyrifos–colloid complexes inhibits the hydrolysis of chlorpyrifos in aqueous systems and that chlorpyrifos–colloid complexes may act as a buffer by slowly releasing chlorpyrifos to the aqueous phase.

INTRODUCTION

Chlorpyrifos is an organophosphorus insecticide that has been widely used in agricultural and urban environments for many years.¹ This compound is characterized by the same P–O–C linkage as in diazinon (diethyl 2-isopropyl-4-methyl-6-pyrimidyl thionophosphate) and parathion (diethyl 4-nitrophenyl thionophosphate). But unlike diazinon² and parathion,³ chlorpyrifos is not affected by accelerated biodegradation in retreated soils. Few microorganisms isolated from environmental matrices have been unequivocally demonstrated to be capable of degrading chlorpyrifos. Microbial enzymes, however, have been shown to hydrolyze chlorpyrifos under controlled conditions.⁴ Racke stated that soil microorganisms most likely play an important role in the complete mineralization of the major chlorpyrifos metabolites such as TCP (3,5,6-trichloro-2-pyridinol) and TMP (trichloro-2-methoxypyridine).⁵

Susceptibility to abiotic hydrolytic degradation is one of the distinguishing features of organophosphate insecticides and is related to their mode of action in cholinesterase enzyme inhibition via phosphorylation.⁵ Most organophosphorus pesticides, including chlorpyrifos, undergo rapid chemical hydrolysis in aqueous systems. Under acidic conditions, pH has little effect on the rate of chlorpyrifos hydrolysis; however, the rate of hydrolysis increases rapidly with increasing pH above pH 7.^{6–8} Meikle and Youngson also reported that the rate of chlorpyrifos hydrolysis increased an average of 3.5-fold for each 10 °C rise in temperature.⁶ Some cations present in aqueous solutions may catalyze cleavage of the P–O bond. For example, Mortland and Raman

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found that the hydrolysis of chlorpyrifos is catalyzed by dissolved Cu ions.⁹

Clays have been found to both promote and inhibit the degradation of pesticides in aqueous and soil systems.⁹⁻¹¹ For organophosphorus pesticides, most evidence indicates that sorption on clay and soil surfaces promotes degradation by catalyzing hydrolysis of the P–O bond.¹²⁻¹⁶ Mingelgrin and Saltzman¹⁶ suggested that a ligand water molecule associated with an exchangeable cation on the clay surface attacks the phosphate ester bond and that the phosphate hydrolysis product forms a stable complex with the exchangeable metal cation. Evidence supporting this mode of action included variation in the rate of parathion hydrolysis on kaolinite with the hydration status of the clay and the nature of the exchangeable cations.¹⁴⁻¹⁶ It has also been reported that sorption on sediments inhibits hydrolysis of chlorpyrifos under alkaline conditions and has no effect on hydrolysis under neutral and acidic conditions.¹⁷ Only limited data for relatively short incubation times were presented in the latter study. Because chlorpyrifos is a widely used insecticide in production agriculture and because many rivers and lakes in agricultural regions have high levels of suspended colloids, we believe that additional investigation of the effects of suspended colloids on the degradation of chlorpyrifos in aqueous systems is needed. The objective of this study was to determine whether adsorption on suspended colloids affects the rate of chlorpyrifos hydrolysis to TCP in aqueous systems.

EXPERIMENTAL SECTION

Chemicals

Reagent grade chlorpyrifos and TCP were obtained from Chem Service (West Chester, PA) with purities of 99.6% and 98.7%, respectively. Ethanol (100%) was used to help dissolve chlorpyrifos for preparation of chlorpyrifos stock solutions. Milli-Q water (Milli-Q plus system, Millipore, Bedford, MA) with a resistivity of 18.2 M Ω -cm was used for preparation of solutions and suspensions.

Colloidal Materials

Otay white montmorillonite (Otay), Panther Creek beidellite (Panther), humic acid (HA), and suspended sediment (Sediment) collected from the Upper Cedar River in north-central Iowa were used for this study. Otay was collected at an exposure near San Diego, CA. Panther was acquired from the A.D. Scott collection, Iowa State University, Ames, IA. The clay fractions (<2 μ m) of Otay and Panther were prepared by sedimentation from their respective bulk ores. The HA was obtained from Aldrich Chemical Company (Milwaukee, WI). Aldrich HA has been criticized as not being representative of soil humic acids; in this study, the Aldrich HA was used as a reference organic colloid. The HA and clays were Ca-saturated by washing 4 times with 1.0 M CaCl₂. The Ca-saturated

samples were dialyzed using Spectra/Por 3500 MWCO molecularporous membrane tubing against Milli-Q water until the conductivity of dialysate was <0.2 mS/m. The Ca-saturated samples were then freeze-dried.

A large volume of river water (~950 L) containing suspended sediment was collected from the Upper Cedar River near Janesville, Iowa on October 16, 1997. The suspended sediment was separated from the river water by freezing-induced flocculation, thawing, and sedimentation. The concentrated suspended sediment sample was then freeze-dried. No chemical treatments were used to prepare the dried suspended sediment sample. The sediment sample contained 105.7 g kg⁻¹ total C (18.4 g kg⁻¹ organic C, 85.1 g kg⁻¹ carbonate C, and 2.2 g kg⁻¹ unidentified C) and 2.8 g kg⁻¹ total N.¹⁸ Particle size analysis indicated that the sediment consisted of 0.9% sand (>0.05 mm), 72.9% silt (0.002–0.05 mm), and 26.2% clay (<0.002 mm).¹⁹ The silt fraction was predominantly calcite while the clay fraction was dominated by smectite with lesser amounts of illite, kaolinite, quartz, and calcite. Mineralogy was determined by X-ray diffraction (XRD) using oriented specimens on glass slides and CuK α radiation with a Siemens D5000 X-ray diffractometer.²⁰

Natural river water from the Upper Cedar River near Janesville, Iowa was collected on December 14, 1999. The river water was filtered using a Whatman 0.2 μ m membrane filter (Whatman, Maidstone, England) to remove suspended particles before it was used in one of the incubation experiments.

Incubation of Chlorpyrifos in Aqueous Systems

Concentrated chlorpyrifos stock solutions were prepared in ethanol and then added to large volumes (8 L) of Milli-Q water, 0.01 M CaCl₂, and filtered (<0.2 μ m) river water to make various chlorpyrifos aqueous solutions. The aqueous solutions contained 0.25% (v/v) ethanol and either 0.257 or 1.283 μ mol L⁻¹ chlorpyrifos. The pH of the aqueous solutions was measured using the Orion Research analog pH meter (model 301). The aqueous solutions were subdivided by putting 450 mL of solution into each of 16 amber glass bottles. The samples were incubated for up to 100 days at 23 \pm 2 $^{\circ}$ C. Periodically during the incubations, whole bottles were sacrificed and the aqueous solutions were analyzed for chlorpyrifos and TCP. Analytes were extracted from the aqueous solutions into tetrahydrofuran (THF) using the solid phase extraction (SPE) technique with Varian (Harbor City, CA) Bond Elut LRC C-18 cartridges. Prior to extraction, the aqueous solutions were adjusted to pH 3.0 using HPLC grade H₃PO₄.

Incubation of Chlorpyrifos in Colloidal Systems

Degradation of chlorpyrifos in dilute colloidal systems was investigated using both low and high concentrations of chlorpyrifos. For the low chlorpyrifos concentration study, the samples contained 0.1 g of colloidal material (Panther, Otay, and Sediment) dispersed in 100 mL 0.01 M CaCl₂, 0.442 μ mol L⁻¹ chlorpyrifos, and 0.02% (v/v) ethanol. The samples were incubated in amber glass bottles at 23 \pm 2 $^{\circ}$ C for up to 100 days. The same amount of chlorpyrifos was also incubated in controls that contained only 0.01 M CaCl₂ and 0.02% (v/v) ethanol. The pH of all systems was measured using the Orion

Research analog pH meter (model 301). The suspensions were periodically shaken using a laboratory shaker. At various times during the incubation, whole bottles were sacrificed and the aqueous phase was analyzed for chlorpyrifos and TCP. For each sample, the suspension was filtered using an Anodisc 0.02- μm membrane filter (Whatman, Maidstone, England) to separate solid from the aqueous phase. Then the analytes in the aqueous phase were extracted into THF using SPE as described above and analyzed by HPLC.

For the concentrated colloidal systems, 0.2 g of colloidal materials (Otay, Panther, HA, and Sediment) were equilibrated with solutions containing 9 mL of 0.01 M CaCl_2 and 1 mL of $107\text{ }\mu\text{g mL}^{-1}$ chlorpyrifos (in ethanol) in Corex glass centrifuge tubes. The suspensions were stored at $23 \pm 2\text{ }^\circ\text{C}$, and were periodically shaken. At various times during the 30-day incubations, samples were sacrificed for analysis of chlorpyrifos and TCP in both the aqueous and solid phases. The aqueous and solid phases were separated by centrifugation ($\times 17,210g$) for 30 min using a DuPont Sorvall RC 28S centrifuge (Wilmington, DE). The analytes in the aqueous phase were extracted into THF using SPE as described above and analyzed by HPLC. For the solid phase remaining in the centrifuge tube, 10 mL of THF was added to the tube and the samples were shaken for 2 h to extract the chlorpyrifos and degradates. The THF extract was separated from the solid using centrifugation ($\times 17,210g$) for 30 min. One milliliter of the extractant was filtered through a 0.02- μm Anotop membrane filter (Whatman, Maidstone, England) to remove ultra-fine particles and then analyzed by HPLC.

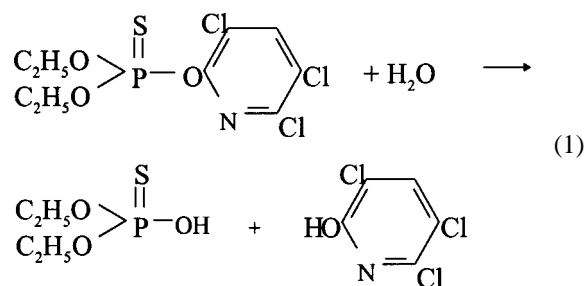
HPLC Analysis

Chlorpyrifos and TCP were quantified using HPLC. The analytes were separated using a reversed-phase SUPELCOSIL LC-18 column ($15.0\text{ cm} \times 4.6\text{ mm i.d.}$) from Supelco (Bellefonte, PA). The mobile phase was HPLC grade acetonitrile and acidified water (pH was adjusted to 3.0 using HPLC grade H_3PO_4). The gradient program started at 10% acetonitrile + 90% water, increased linearly to 90% acetonitrile + 10% water over 20 min, held for 5 min, and then returned to the initial state in 5 min. A 50- μL sample injection loop was used and the flow rate was 1.0 mL min^{-1} . The analytes were detected with a Hewlett Packard (series 1100) diode array UV-Vis detector. Retention times were 19.8 min for chlorpyrifos and 12.1 min for TCP. Chlorpyrifos and TCP were quantified at 230 and 302 nm, respectively. Linear calibration curves with correlation coefficients (r^2) of 0.9999 were achieved for chlorpyrifos and TCP over concentration ranges of 0 to 0.5 mmol L^{-1} and 0 to 0.25 mmol L^{-1} , respectively.

RESULTS AND DISCUSSION

Hydrolysis of Chlorpyrifos in Aqueous Systems

A general hydrolytic reaction (eq 1) of chlorpyrifos in water involves cleavage of the phosphorothioate ester bond to form TCP.⁵ Other degradation products of chlorpyrifos, including chlorpyrifos-oxon [*O,O*-diethyl *O*-(3,5,6-trichloro-2-pyridyl) phosphate] and desethyl chlorpyrifos [*O*-ethyl *O*-(3,5,6-trichloro-2-pyridyl)



phosphorothioate], also readily hydrolyze to TCP. The hydrolysis of chlorpyrifos to TCP is believed to follow simple second-order kinetics, which is first-order with respect to chlorpyrifos concentration and first-order with respect to hydroxyl concentration.⁸ For constant pH, the reaction rate is described by a pseudo-first-order equation

$$-\frac{dC_t}{dt} = K C_t \quad (2)$$

where C_t is the concentration of chlorpyrifos at time t . Integration of eq 2 yields:

$$\log C_t = \log C_0 - \frac{K}{2.303} t \quad (3)$$

where C_0 is the concentration of chlorpyrifos at time zero. Figure 1 shows the relationship between $\log C_t$ and time (t) for Milli-Q water, 0.01 M CaCl_2 , and filtered Cedar River water. The linear relationships imply that the degradation of chlorpyrifos fits fairly well in pseudo-first-order kinetics, and the first-order rate constants (Table 1) indicate similar hydrolysis rates for the low initial concentration of chlorpyrifos in 0.01 M CaCl_2 and Milli-Q water and for the high initial concentration of chlorpyrifos in 0.01 M CaCl_2 . However, the rate constant for the high initial chlorpyrifos concentration in Milli-Q water was 2.8 times smaller than the rate constant for the low initial concentration in Milli-Q water, and the rate constant for the filtered Cedar River water is 1.4 times larger for the high initial concentration system than the low initial concentration system. The observed effect of initial concentration for the Milli-Q water and filtered Cedar River water systems suggests that pseudo-first order kinetics may not describe degradation of chlorpyrifos in aqueous systems over a large concentration range.

During the incubations, concentrations of TCP were also measured (Fig. 2). TCP concentrations increased over time, but the increase could not account for all of the chlorpyrifos that disappeared from the aqueous systems. Loss of chlorpyrifos due to volatilization was minimized by keeping the sample bottles tightly sealed during the incubations. In natural environments, TCP is degraded via photolysis²¹ and microbial degradation.²²

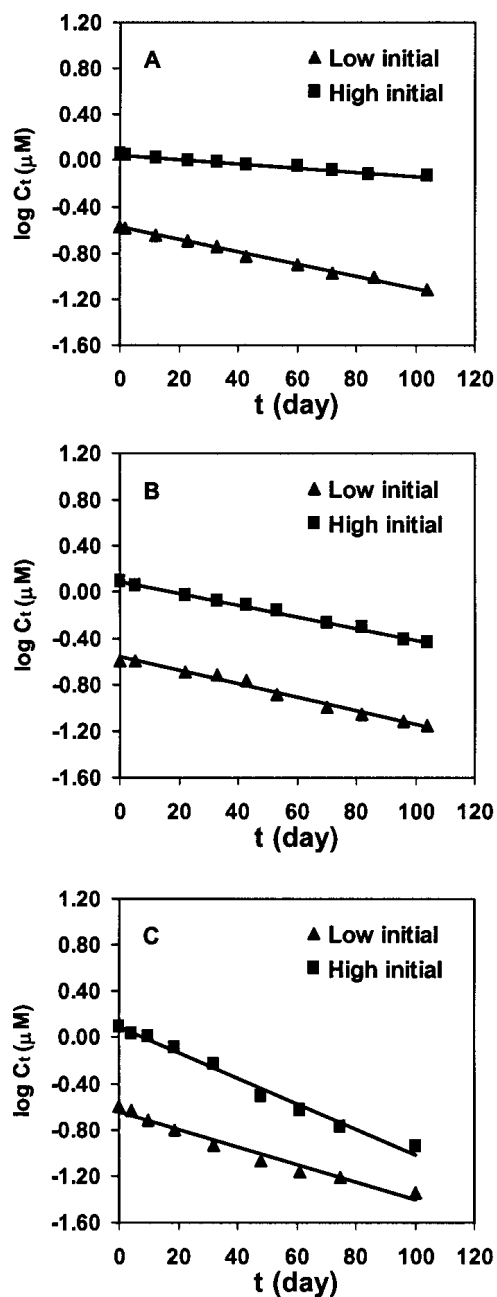


Fig. 1. First-order plots of chlorpyrifos hydrolysis in aqueous systems. A: Milli-Q water; B: 0.01 M CaCl_2 ; C: filtered Cedar River water. Low and high initial concentrations of chlorpyrifos were 0.257 and 1.283 $\mu\text{mol L}^{-1}$, respectively.

In our experiments, photolysis was inhibited by the use of amber glass bottles. Although our experiments were not run under sterile conditions, minimal microbial activity was anticipated because the only sources of nutrients in the samples were ethanol, chlorpyrifos, and any degradation products. TCP was not detectable in the filtered Cedar River water systems (Fig. 2) until day 45 in the low initial chlorpyrifos concentration system and not until day 20 in the high initial chlorpyrifos concentration system. By contrast, TCP was clearly detected on or before day 20 in all of the Milli-Q water and 0.01 M CaCl_2 systems. The cause of the delay in TCP appearance in the filtered Cedar River water is not clear, but suggests an initial rapid degradation reaction that does not involve production of TCP.

The pH values of Milli-Q water, 0.01 M CaCl_2 , and filtered Cedar River water were 6.50, 6.30, and 8.05, respectively. The higher pH of the filtered Cedar River water clearly favors alkaline hydrolysis of chlorpyrifos and explains the higher rate constants for the filtered Cedar River water relative to the Milli-Q water and 0.01 M CaCl_2 systems (Table 1). However, pH cannot explain the effect of initial chlorpyrifos concentration, the lack of stoichiometry between chlorpyrifos and TCP, or the apparent delay in appearance of TCP for the filtered Cedar River water systems. These factors all suggest that the degradation of chlorpyrifos in aqueous systems is more complex than the simple hydrolysis reaction (eq 1). No chlorpyrifos-oxon was detected, but otherwise no attempt was made in this study to identify and quantify other degradation compounds. Degradation of chlorpyrifos in the filtered Cedar River water systems may have been influenced by dissolved metals. Mortland and Raman reported nearly 100% hydrolysis of chlorpyrifos (2.8 mg L^{-1}) within 24 h in aqueous methanol (50% v/v) containing 0.1 mM Cu^{2+} , limited hydrolysis (10% in 24 h) in the presence of 0.1 mM MgCl_2 , and negligible hydrolysis in the presence of CaCl_2 .⁹ The filtered Cedar River water was dominated by Ca but also contained Al, Mg, Fe, Mn, and Na, as detected by a quick scan using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Although there is little evidence in the literature for microbial degradation of chlorpyrifos, the possibility cannot be entirely discounted.

Table 1. Kinetic parameters for chlorpyrifos hydrolysis in aqueous systems

aqueous system	pH	low initial concentration		high initial concentration	
		K (day^{-1})	$t_{1/2}$ (days)	K (day^{-1})	$t_{1/2}$ (days)
Milli-Q water	6.50	0.0122	56.8	0.0044	157.5
0.01 M CaCl_2	6.30	0.0131	52.9	0.0115	60.3
filtered Cedar River water	8.05	0.0177	39.2	0.0256	27.1

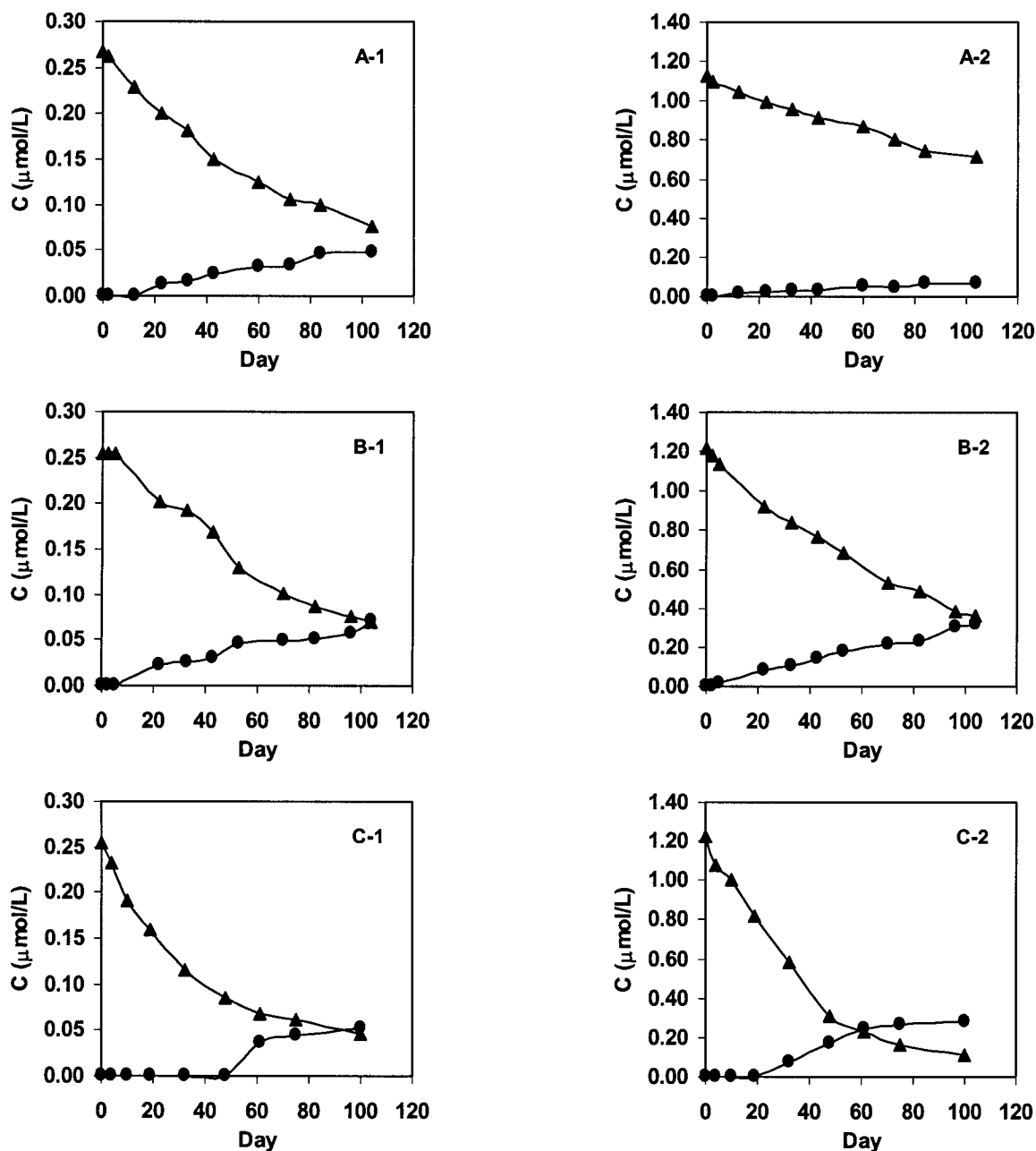


Fig. 2. Disappearance of chlorpyrifos (triangles) and appearance of TCP (circles) in aqueous solutions as a function of time. A-1: low initial concn in Milli-Q water; A-2: high initial concn in Milli-Q water; B-1: low initial concn in 0.01 M CaCl_2 ; B-2: high initial concn in 0.01 M CaCl_2 ; C-1: low initial concn in filtered Cedar River water; C-2: high initial concn in filtered Cedar River water.

Degradation of Chlorpyrifos in Dilute Colloidal Systems

Disappearance of chlorpyrifos from the aqueous phase in the dilute colloidal systems (1 g L^{-1} in 0.01 M CaCl_2) is illustrated in Fig. 3 and the appearance of TCP in the systems is illustrated in Fig. 4. At time zero, the aqueous phase concentrations of chlorpyrifos were lower in the colloidal suspensions than in the control

(0.01 M CaCl_2) due to sorption of chlorpyrifos on the suspended solids. However, during the incubations chlorpyrifos disappeared relatively slower from the aqueous phase in the colloidal systems than from the aqueous phase in the control. After 60 days, aqueous phase concentrations of chlorpyrifos in the Panther and Otay systems were actually higher than the concentrations in the control. In the Sediment system, chlorpyrifos

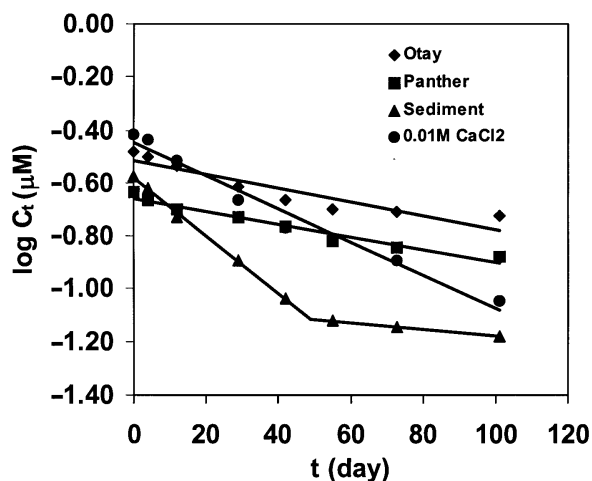


Fig. 3. First-order plots of degradation of chlorpyrifos in dilute colloidal systems (1 g L^{-1}). The same amount of chlorpyrifos was present in all systems at time zero. Differences relative to the control (0.01 M CaCl_2) in aqueous concentrations of chlorpyrifos at time zero are due to sorption of chlorpyrifos by the suspended colloids.

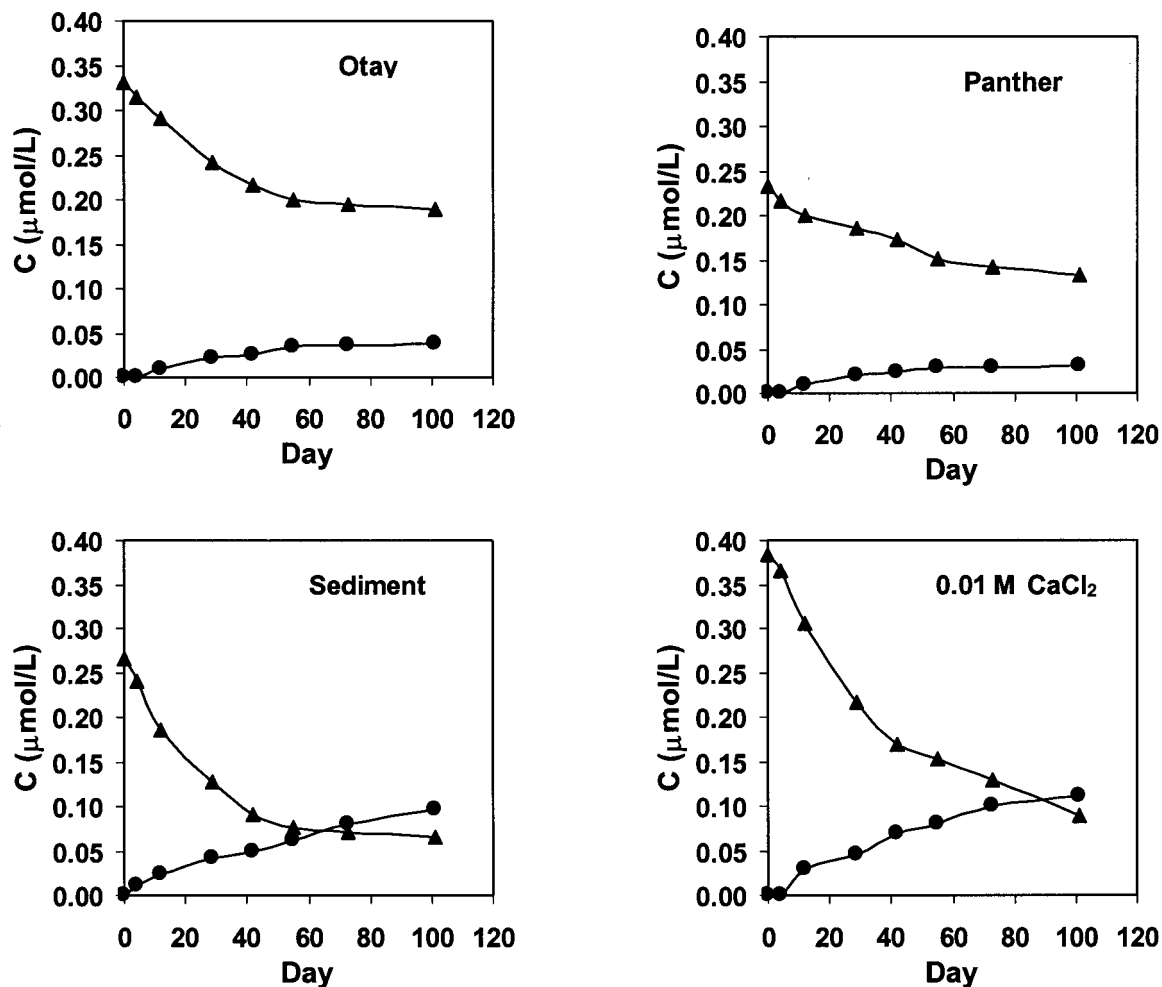


Fig. 4. Disappearance of chlorpyrifos (▲) and appearance of TCP (●) in dilute colloidal systems (1 g L^{-1}) as a function of time. Differences in initial concentrations of chlorpyrifos relative to the control (0.01 M CaCl_2) at time zero are due to sorption by the suspended colloids.

Table 2. Kinetic parameters for chlorpyrifos hydrolysis in dilute colloidal systems

systems	pH	K day ⁻¹	t _{1/2} days
Otay-suspension	5.75	0.0060	115.5
Panther-suspension	5.46	0.0055	126.0
Sediment-suspension	8.02	0.0251	27.6
0.01 M CaCl ₂ solution	6.30	0.0120	57.8

disappeared rapidly from the aqueous phase during the first 50 days of incubation; however, after 50 days the aqueous phase concentrations stabilized. The measured first-order t_{1/2} for chlorpyrifos in the Otay, Panther, and control systems over 100 days of incubation are 115.5, 126.0, and 57.8 days, respectively (Table 2). TCP increased with incubation time for all of the dilute colloidal systems (Fig. 4), however, levels of TCP were always well below that needed to account for the disappearance of chlorpyrifos. Concentrations of TCP in the Panther and Otay systems were less than half those observed in the Sediment and 0.01 M CaCl₂ systems. The relatively long t_{1/2} values and the low levels of TCP

observed for the Otay and Panther systems indicate that sorption on the suspended smectites limited hydrolysis of chlorpyrifos in these system.

Macalady and Wolfe¹⁷ reported that sorption on sediments has no effect on hydrolysis of chlorpyrifos under acidic and neutral conditions but substantially reduces the rate of hydrolysis under alkaline conditions. In the present study, the pH values in Panther, Otay, and 0.01 M CaCl₂ systems were 5.46, 5.75, and 6.30, respectively. Therefore, our results demonstrate that sorption on suspended smectites inhibits hydrolysis of chlorpyrifos even under mildly acidic conditions. Our results also demonstrate that the presence of suspended smectites may stabilize aqueous phase concentrations of chlorpyrifos during extended incubations. The higher pH in the Sediment system (8.02), due to the presence of carbonates, promoted alkaline hydrolysis of chlorpyrifos.

Degradation of Chlorpyrifos in Concentrated Colloidal Systems

To quantify transformation of chlorpyrifos occurring on the surface of colloidal materials, a relatively larger amount of chlorpyrifos was added to colloid-water systems with a high solid-to-water ratio. Tables 3–6 present

Table 3. Distribution of chlorpyrifos in the aqueous and solid phases in the concentrated Otay system

time (day)	chlorpyrifos _{aqueous} (μmol L ⁻¹)	chlorpyrifos _{solid} (μmol g ⁻¹)	recovery [†] (%)	TCP (μmol L ⁻¹)
1	6.33	1167	97	nd [‡]
5	4.48	1215	97	nd
10	4.25	1115	89	nd
15	4.65	1081	88	nd
20	4.91	1095	90	nd
25	5.19	1030	87	nd
30	5.45	947	82	nd

[†]Recovery (%) denotes the sum of chlorpyrifos extracted by THF from the solid phase and chlorpyrifos measured in the aqueous phase as a percentage of the total amount of chlorpyrifos added initially in the system.

[‡]Not detectable in either aqueous or solid phase.

Table 4. Distribution of chlorpyrifos in the aqueous and solid phases in the concentrated Panther system

time (day)	chlorpyrifos _{aqueous} (μmol L ⁻¹)	chlorpyrifos _{solid} (μmol g ⁻¹)	recovery [†] (%)	TCP (μmol L ⁻¹)
1	1.82	1263	92	nd [‡]
5	1.83	1263	92	nd
10	1.88	1281	93	nd
15	1.85	1246	91	nd
20	1.89	1241	90	nd
25	2.19	1215	89	nd
30	1.87	1201	87	0.17

[†]See Table 3.

[‡]Not detectable. For day 30, trace TCP was detected in the aqueous phase.

Table 5. Distribution of chlorpyrifos in the aqueous and solid phases in the concentrated Sediment system

time (day)	chlorpyrifos _{aqueous} ($\mu\text{mol L}^{-1}$)	chlorpyrifos _{solid} ($\mu\text{mol g}^{-1}$)	recovery [†] (%)	TCP ($\mu\text{mol L}^{-1}$)
1	4.05	1044	84	nd [‡]
5	3.91	1067	85	nd
10	3.91	1061	84	nd
15	4.16	1041	84	nd
20	4.76	967	81	nd
25	4.48	955	80	nd
30	3.74	981	78	nd

^{†,‡}See Table 3.

Table 6. Distribution of chlorpyrifos in the aqueous and solid phases in HA system

time (day)	chlorpyrifos _{aqueous} ($\mu\text{mol L}^{-1}$)	chlorpyrifos _{solid} ($\mu\text{mol g}^{-1}$)	recovery [†] (%)	TCP ($\mu\text{mol L}^{-1}$)
1	0.29	1435	97	nd [‡]
5	0.17	1255	86	nd
10	0.14	1272	87	nd
15	0.20	1232	83	nd
20	0.20	1172	79	nd
25	0.17	1155	79	nd
30	0.17	1158	79	nd

^{†,‡}See Table 3.

the distribution of chlorpyrifos in the aqueous and solid phases for four different colloidal systems as a function of incubation time. In these systems, chlorpyrifos was dominantly adsorbed on the colloids. However, some chlorpyrifos remained in the aqueous phase, depending on the affinities of the various colloids for chlorpyrifos. The concentrations of chlorpyrifos in the aqueous phases varied from 0.14 $\mu\text{mol L}^{-1}$ for the HA system to 6.33 $\mu\text{mol L}^{-1}$ for the Otay system. This is consistent with the report that chlorpyrifos has a strong tendency to be adsorbed by organic material due to its nonpolar nature.⁵ However, the concentration of chlorpyrifos in the aqueous phase of the colloid-water systems did not decrease during the 30-day incubations, as would be expected for the degradation of chlorpyrifos in aqueous systems.

Total recoveries for chlorpyrifos extracted from the solid phase and measured in the aqueous phase on day 30 of the incubations were 82%, 87%, 78%, and 79% for the Otay, Panther, Sediment, and HA systems, respectively. The percent recoveries for the concentrated colloidal systems are substantially higher than the percent recoveries for either the aqueous or the dilute colloidal systems on day 30 of those incubations. Furthermore, during the 30-day incubation, TCP did not appear in

either the aqueous or solid phase of the concentrated Otay, Sediment, and HA systems and only a trace amount of TCP (0.17 $\mu\text{mol L}^{-1}$) was detected on day 30 in the aqueous phase of the Panther system. By contrast, TCP was clearly present before day 30 in all of the aqueous (Fig. 2) and dilute colloidal (Fig. 4) systems with the exception of the low initial concentration-filtered Cedar River water system. Results for the concentrated colloidal systems provide further evidence that sorption on suspended colloids inhibits degradation of chlorpyrifos and nearly stops the hydrolysis of chlorpyrifos to TCP. The slow disappearance of chlorpyrifos from the concentrated colloidal systems with incubation time suggests that chlorpyrifos was either transformed to a degradation product(s) other than TCP or that chlorpyrifos formed a tightly-bound residue with the colloidal materials that could not be extracted with THF.

Base catalyzed hydrolysis of chlorpyrifos to TCP is a major pathway for the degradation of chlorpyrifos.^{5,8} However, the results of this study suggest that other degradation pathways that do not involve TCP are also important and that the hydrolysis to TCP is substantially or even completely inhibited by adsorption of chlorpyrifos on colloidal materials. The chemical environments of the aqueous and solid phases in colloidal

systems differ greatly.²³ Anions, including hydroxyls, are electrostatically repulsed from smectite surfaces due to the dominance of negative surface charge. As a result, the surfaces of suspended colloids are effectively 1 to 2 pH units lower than the bulk solution.²⁴ Therefore, it is reasonable to speculate that chlorpyrifos adsorbed on smectite surfaces is more stable than dissolved chlorpyrifos because the adsorbed chlorpyrifos is less exposed to hydroxide ions. Similarly, chlorpyrifos sorbed on humic acid macromolecules may be sequestered within hydrophobic domains where the chlorpyrifos is protected from exposure to hydroxide ions.

CONCLUSIONS

The rate of chlorpyrifos hydrolysis to TCP was affected by both water chemistry and by the presence and nature of suspended colloids in aqueous systems. None of the colloidal materials used in this study catalyzed the hydrolysis of chlorpyrifos to TCP in 0.01 M CaCl₂ aqueous systems. On the contrary, sorption of chlorpyrifos on colloidal materials reduced the rate of chlorpyrifos degradation and apparently stopped the hydrolysis of chlorpyrifos to TCP. The results suggest that sorption of chlorpyrifos on suspended colloids may act as a buffer to maintain low levels of chlorpyrifos in the aqueous phase both by retarding degradation and by slowly releasing adsorbed chlorpyrifos to the aqueous phase as chlorpyrifos in the aqueous phase is degraded. Further study is needed to elucidate degradation mechanisms other than hydrolysis to TCP, which are responsible for the disappearance of chlorpyrifos from aqueous and colloidal systems.

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